CONCEPT MAP

CLASS XI

Trends and Anomalies in s- and p-Block Elements

Generally in a group, elements show a regular trend in their physical and chemical properties with increase in their atomic numbers. But some of the elements show exceptional behaviour and anomalies.

General Trends in Properties of s- and p-Block Compounds

Carbonates and Bicarbonates Stability

- $Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$
- $LiHCO_3 < NaHCO_3 < KHCO_3 < RbHCO_3 < CsHCO_3$
- $BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$

Basic Strength, Solubility and Stability of Hydroxides

- $LiOH < NaOH < KOH < RbOH < CsOH$
- $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$
- $\underbrace{B(OH)_3}_{\text{Acidic}} < \underbrace{Al(OH)_3 < Ga(OH)_3}_{\text{Amphoteric}} < \underbrace{In(OH)_3 < Tl(OH)_3}_{\text{Basic}}$

Solubility and Basic Strength of Oxides

- $Li_2O < Na_2O < K_2O < Rb_2O < Cs_2O$
- $\underbrace{BeO}_{\text{Amphoteric}} < \underbrace{MgO}_{\text{Weakly basic}} < \underbrace{CaO < SrO < BaO}_{\text{Strongly basic}}$
- $\underbrace{B_2O_3}_{\text{Weakly acidic}} < \underbrace{Al_2O_3 < Ga_2O_3}_{\text{Amphoteric}} < \underbrace{In_2O_3 < Tl_2O_3}_{\text{Basic}}$

Stability of Peroxides and Superoxides

- $Na_2O_2 < K_2O_2 < Rb_2O_2 < Cs_2O_2$
- $NaO_2 < KO_2 < RbO_2 < CsO_2$
- $MgO_2 < CaO_2 < SrO_2 < BaO_2$

Solubility in Water

- $LiF < NaF < KF < RbF < CsF$
- $LiCl < NaCl < KCl < RbCl < CsCl$
- $NaF < NaCl < NaBr < NaI$
- $BeCl_2 > MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$
- $BF_3 < BCl_3 < BBr_3$

Stability of Halides

- $CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$
- $CF_4 > CCl_4 > CBr_4 > CI_4$
- $PbX_2 > SnX_2 > GeX_2 > SiX_2$

Solubility of Sulphates

- $BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$

Stability of Sulphate

- $BeSO_4 < MgSO_4 < CaSO_4 < SrSO_4$

Anomalous Behaviour of First Element of Group

Due to

- Small size
- High electronegativity
- High ionization enthalpy
- Absence of *d*-orbitals in valence shell

Anomalous Behaviour of Lithium

- Melting and boiling points are comparatively high.
- Lithium forms nitride while other alkali metals do not.
  $6Li + N_2 \rightarrow 2Li_3N$
- Lithium hydroxide and carbonate decompose on heating, while other alkali metal hydroxides and carbonates do not.
  $2LiOH \xrightarrow{\Delta} Li_2O + H_2O$ $\quad Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2\uparrow$

Anomalous Behaviour of Beryllium

- Beryllium is harder than other group members.
- Beryllium does not react with water even at high temperature.
- Beryllium forms covalent compounds. Because of covalent character salts of beryllium are easily hydrolysed.
  $BeCO_3 + 4H_2O \rightarrow [Be(H_2O)_4]^{2+} + CO_3^{2-}$

Anomalous Behaviour of Boron

- Boron is hard and has high melting and boiling points.
- Boron forms only covalent compounds while others form both ionic and covalent compounds.
- The oxide and hydroxide of boron are weakly acidic.
  $B_2O_3 + 2NaOH \rightarrow 2NaBO_2 + H_2O$
  $B(OH)_3 + NaOH \rightarrow NaBO_2 + 2H_2O$

Anomalous Behaviour of Carbon

- Due to small size and high electronegativity, carbon has a strong tendency to form $p\pi$-$p\pi$ multiple bonds.
- Carbon has high tendency of catenation. Tendency for catenation : $C >> Si > Ge \approx Sn >> Pb$

Stability of Hydrides

- $LiH > NaH > KH > RbH > CsH$
- $CH_4 > SiH_4 > GeH_4 > SnH_4 > PbH_4$

Lewis Acid Character

- $BI_3 > BBr_3 > BCl_3 > BF_3$

Stability of Nitrates

- $Be(NO_3)_2 < Mg(NO_3)_2 < Ca(NO_3)_2 < Sr(NO_3)_2 < Ba(NO_3)_2$

Applications of Colloids

Colloids have very vast applications from food products to industries like rubber etc.

In Nature and Everyday Life

Food Articles

Number of food articles that we eat, are colloidal in nature, *e.g.*,
- **Milk :** Fat dispersed in water.
- **Bread :** Air dispersed in baked dough.

Medicines

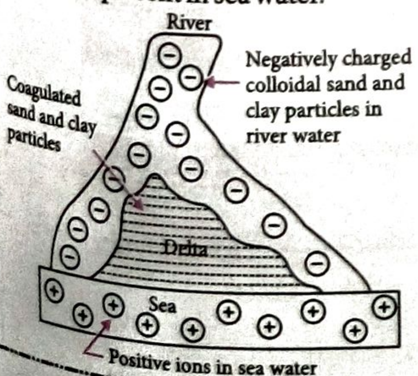
- Colloidal medicines are more effective as they are easily absorbed in the body, *e.g.*,
  - **Silver colloid :** Germicidal
  - **Copper colloid :** Anticancer
  - **Mercury colloid :** Antisyphilis
- Colloidal dispersion of gelatin is used in coating over tablets and granules.

Blood Coagulation

Blood consists of negatively charged colloidal particles (albuminoid substances). On applying ferric chloride solution, it causes coagulation of blood to form a clot which stops further bleeding.

Formation of Delta

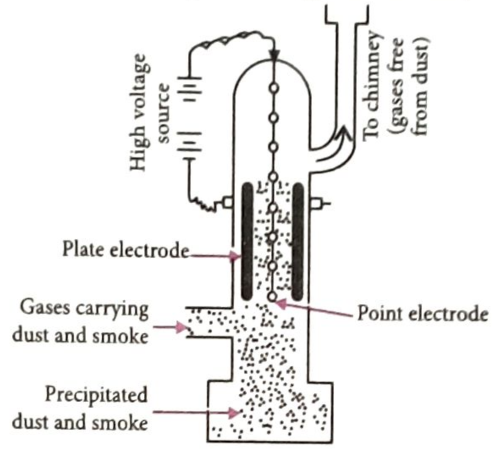
Formation of delta shaped heap of sand, clay, etc. where river falls into sea due to coagulation of sand/clay particles by electrolytes present in sea water.



In Industries

Smoke Precipitation

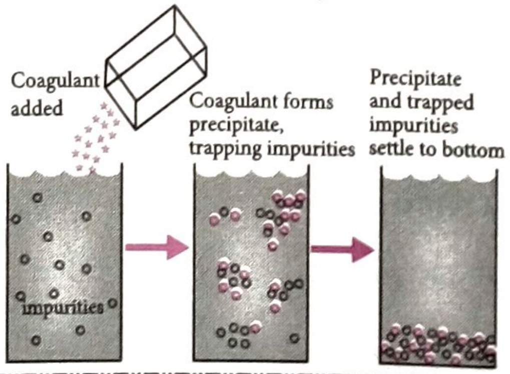
Smoke is a big problem for environment as it is the major cause of air pollution. Coagulation of the dispersed colloidal particles (smoke) occurs on metal plates before allowing them to pass through the chimney.



Cottrell Precipitator

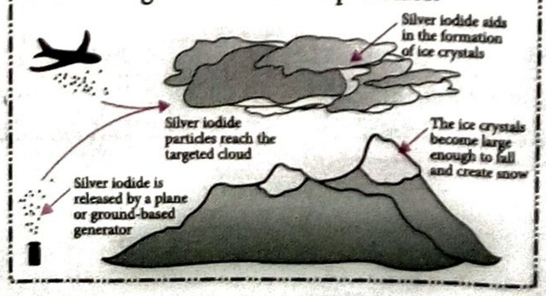
Purification of Drinking Water

Addition of the electrolyte (like alum) for water purification is based on the fact that impure water is a colloidal system.



Artificial Rain

Due to mixing of oppositely charged sand or common salt with the clouds to bring about coagulation of water particles.



Applications of Adsorption

Adsorption finds extensive applications in research laboratories and in industries. It can be used to remove certain classes of pollutants from air and industrial waste water.

In Gas Masks

Gas masks are used to adsorb poisonous gases (*e.g.*, Cl_2, CO, oxides of sulphur etc.) and thus purify the air for breathing. Activated charcoal is used for this purpose.

Removal of Colouring Matter from Solution

Many substances such as sugar, juice and vegetable oils (having coloured impurities) can be decolourised by using adsorbents like activated charcoal or fuller's earth, *e.g.*, animal charcoal is used as a decolouriser in the manufacture of cane sugar.

Heterogeneous Catalysis

Mostly heterogeneous catalytic reactions proceed through the adsorption of gaseous reactants on solid catalyst, *e.g.*,
- Finely powdered nickel is used for the hydrogenation of oils.
- Finely divided vanadium pentaoxide (V_2O_5) is used in the Contact process for the manufacture of sulphuric acid.

In Curing Disease

Some drugs can adsorb the germs and kill them hence, save us from diseases.

Separation of Inert Gases

Due to the difference in degree of adsorption of gases by charcoal, a mixture of inert gases can be separated by adsorption on coconut charcoal at different temperatures.

Chemistry of f-Block Elements

The elements in which the last electron enters the anti-penultimate energy level, *i.e.*, $(n - 2)$ f-orbitals, are called f-block or inner transition elements.

General electronic configuration : $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$

Lanthanoids

The elements in which the last electron enters one of the 4f-orbitals, are called lanthanides or lanthanons.

Name of the elements	Symbol (Ln)	At. No. (Z)	Electronic configuration	Oxidation states
Lanthanum	La	57	$[Xe]\,5d^16s^2$	$+\underline{3}$
Cerium	Ce	58	$[Xe]4f^15d^16s^2$	$+\underline{3}, +4$
Praseodymium	Pr	59	$[Xe]4f^3\,5d^06s^2$	$+\underline{3}, +4$
Neodymium	Nd	60	$[Xe]4f^45d^06s^2$	$+2, +\underline{3}, +4$
Promethium	Pm	61	$[Xe]4f^55d^06s^2$	$+\underline{3}$
Samarium	Sm	62	$[Xe]4f^65d^06s^2$	$+2, +\underline{3}$
Europium	Eu	63	$[Xe]4f^75d^06s^2$	$+2, +\underline{3}$
Gadolinium	Gd	64	$[Xe]4f^75d^16s^2$	$+\underline{3}$
Terbium	Tb	65	$[Xe]4f^95d^06s^2$	$+\underline{3}, +4$
Dysprosium	Dy	66	$[Xe]4f^{10}5d^06s^2$	$+\underline{3}, +4$
Holmium	Ho	67	$[Xe]4f^{11}5d^06s^2$	$+\underline{3}$
Erbium	Er	68	$[Xe]4f^{12}5d^06s^2$	$+\underline{3}$
Thulium	Tm	69	$[Xe]4f^{13}5d^06s^2$	$+2, +\underline{3}$
Ytterbium	Yb	70	$[Xe]4f^{14}5d^06s^2$	$+2, +\underline{3}$
Lutetium	Lu	71	$[Xe]\,4f^{14}5d^16s^2$	$+\underline{3}$

*Underlined oxidation states are stable.

Lanthanoid Contraction

Lanthanoid contraction

The regular decrease in atomic and ionic radii of lanthanoids with increasing atomic number, is known as lanthanoid contraction.

Cause of lanthanoid contraction

Lanthanoid contraction is caused due to increase in nuclear charge which outweighs the imperfect shielding of f-electrons.

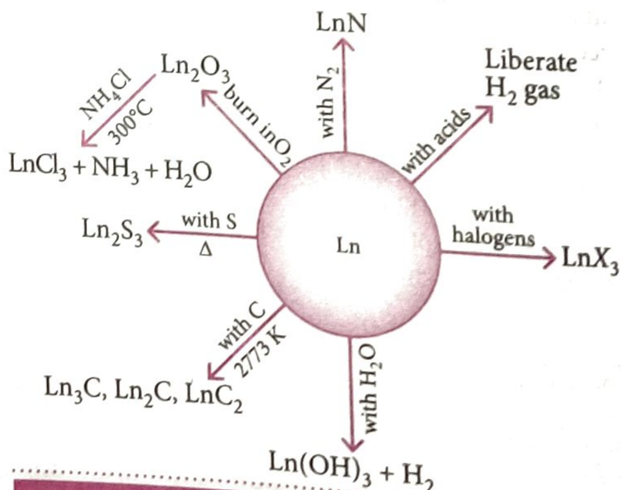
Consequences of lanthanoid contraction

Due to decrease in size from La^{3+} to Lu^{3+}, the basic strength of their hydroxides decreases.

Due to similarity in size, 2nd and 3rd rows of transition elements resemble each other more closely than do the first and second rows.

Due to almost same ionic radii, their chemical properties are similar. Hence, these are difficult to separate.

Chemical Properties of Lanthanoids



Actinoids

Name of the elements	Symbol	At. No. (Z)	Electronic configuration	Oxidation states
Actinium	Ac	89	$[Rn]6d^1, 7s^2$	$+\underline{3}$
Thorium	Th	90	$[Rn]6d^2, 7s^2$	$+3, +\underline{4}$
Protactinium	Pa	91	$[Rn]5f^2, 6d^1, 7s^2$	$+3, +4, +\underline{5}$
Uranium	U	92	$[Rn]5f^3, 6d^1, 7s^2$	$+3, +4, +5, +\underline{6}$
Neptunium	Np	93	$[Rn]5f^4, 6d^1, 7s^2$	$+3, +4, +\underline{5}, +6, +7$
Plutonium	Pu	94	$[Rn]5f^6, 6d^0, 7s^2$	$+3, +\underline{4}, +5, +6, +7$
Americium	Am	95	$[Rn]5f^7, 6d^0, 7s^2$	$+\underline{3}, +4, +5, +6$
Curium	Cm	96	$[Rn]5f^7, 6d^1, 7s^2$	$+\underline{3}, +4$
Berkelium	Bk	97	$[Rn]5f^9, 6d^0, 7s^2$	$+\underline{3}, +4$
Californium	Cf	98	$[Rn]5f^{10}, 6d^0, 7s^2$	$+2, +\underline{3}$
Einsteinium	Es	99	$[Rn]5f^{11}, 6d^0, 7s^2$	$+2, +\underline{3}$
Fermium	Fm	100	$[Rn]5f^{12}, 6d^0, 7s^2$	$+2, +\underline{3}$
Mendelevium	Md	101	$[Rn]5f^{13}, 6d^0, 7s^2$	$+2, +\underline{3}$
Nobelium	No	102	$[Rn]5f^{14}, 6d^0, 7s^2$	$+2, +3$
Lawrencium	Lr	103	$[Rn]5f^{14}, 6d^1, 7s^2$	$+\underline{3}$

*Underlined oxidation states are stable.

Comparison of Lanthanoids and Actinoids

Similarities

- The elements of both the series show mainly +3 oxidation state.
- The elements of both the series are electropositive in nature. They are reactive metals and act as strong reducing agents.
- Actinoids exhibit actinoid contraction like lanthanoid contraction. These contractions are due to the poor shielding effect of electrons residing in $(n-2)$ f-orbitals.
- Cations with unpaired electrons in both the series are paramagnetic.

Dissimilarities

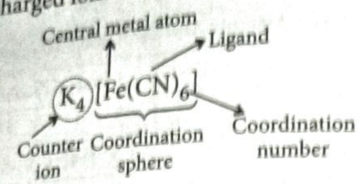
S.N.	Lanthanoids	Actinoids
1.	Except promethium, all the remaining lanthanides are non-radioactive.	All the actinides are radioactive.
2.	Besides +3 oxidation state, lanthanides in some cases show +2 and +4 oxidation states.	Besides +3 oxidation state, actinides show a variety of oxidation states like +2, +4, +5, +6 and +7.
3.	Oxides and hydroxides of lanthanides are less basic.	Oxides and hydroxides of actinides are more basic.
4.	Most of the tripositive ions are colourless.	Most of the tripositive and tetrapositive ions are coloured.

INFO SHOTS

Transition Metal Silicides !

Transition metal silicides, a distinct class of semiconducting materials that contain silicon, demonstrate superior oxidation resistance, high temperature stability and low corrosion rates, which make them promising for a variety of future developments in electronic devices.

- A coordination compound contains a central metal atom or ion surrounded by a number of oppositely charged ions or neutral molecules, called ligands.



Types of Ligands

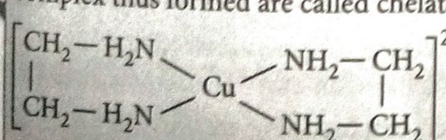
Monodentate
Only one donor atom is present, *e.g.*, NH_3, H_2O, CN^-, NO_2^-, CO

Bidentate
Two donor atoms are present, *e.g*, ethylenediamine (*en*)
$CH_2-\ddot{N}H_2$
|
$CH_2-\ddot{N}H_2$
oxalato (*ox*) COO^-
|
COO^-

Tridentate
Three donor atoms are present, *e.g.*,
$H\ddot{N}\begin{cases}(CH_2)_2\ddot{N}H_2\\(CH_2)_2\ddot{N}H_2\end{cases}$
Diethylenetriamine (*dien*)

Polydentate
Tetradentate : Triethylenetetraamine (*trien*)
Pentadentate : Ethylenediaminetriacetate ion
Hexadentate : Ethylenediaminetetraacetate ion (EDTA)

Chelating ligands
A bidentate or a polydentate ligand is known as chelating ligand if on coordination it results in the formation of a closed or cyclic ring structure. The complex thus formed are called chelates.

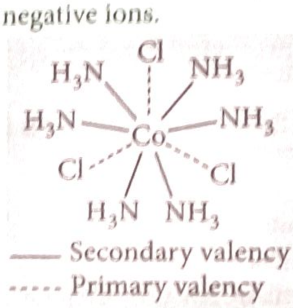


EAN Rule

EAN = Z – O.N + 2(C.N)
Z = Atomic number of central metal atom
O.N. = Oxidation number of central metal atom
C.N. = Coordination number of central metal atom

Werner's Theory

- Metal possesses two types of valencies, *i.e.*, primary valency (ionisable) and secondary valency (non-ionisable).
- Primary valency corresponds to the oxidation state of the central metal and secondary valency represents the coordination number of the metal.
- Primary valencies are satisfied by negative ions, while secondary valencies may be satisfied by neutral or negative ions.



- Negative ion can satisfy both primary and secondary valencies at the same time.

Nomenclature of Coordination Compounds

Rules for nomenclature :

- Positive ion is named first followed by negative ion.
- Negative ligands are named by adding suffix – o.
- Positive ligands are named by adding suffix – ium.
- Neutral ligands are named as such without adding any suffix or prefix.
- Ligands are named in alphabetical order.
- Name of the ligands is written first followed by name of metal with its oxidation number mentioned in roman numerals in simple parenthesis.
- Number of the polysyllabic ligands *i.e.*, ligands which have numbers in their name, is indicated by prefixes bis, tris, tetrakis, etc.
- When both cation and anion are complex ions, the metal in negative complex is named by adding suffix -ate.

Ligand	Name in complexes	Ligand	Name in complexes
Azide (N_3^-)	Azido	Oxalate ($C_2O_4^{2-}$)	Oxalato
Bromide (Br^-)	Bromido	Oxide (O^{2-})	Oxo
Chloride (Cl^-)	Chlorido	Ammonia (NH_3)	Ammine
Cyanide (CN^-)	Cyano	Carbon monoxide (CO)	Carbonyl
Fluoride (F^-)	Fluorido	Ethylene-diamine (*en*)	Ethylene-diamine

Hydroxide (OH^-)	Hydro	(C_5H_5N)	
Carbonate (CO_3^{2-})	Carbonato	Water (H_2O)	Aqua

Few examples illustrate the nomenclature :

- $[Pt(NH_3)_6]Cl_4$ – Hexaammineplatinum(IV) chloride
- $[Cu(en)_2]SO_4$ – *bis*(ethane-1,2-diamine)copper(II) sulphate
- $K_4[Fe(CN)_6]$ – Potassium hexacyanoferrate(II)
- $[Pt(NH_3)_4Cl_2][PtCl_4]$ – Tetraamminedichlorido-platinum(IV) tetrachloridoplatinate(II)

Isomerism in Coordination Compounds

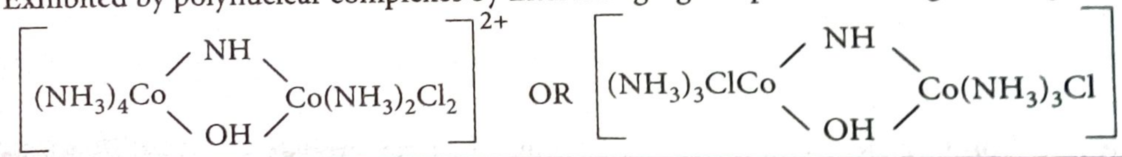
Stereoisomerism

Structural Isomerism

Ionisation isomerism
- Isomerism arises in the compounds which have same molecular formula but give different ions in solution, *e.g.*, $[Co(NH_3)_5Br]SO_4$, $[Co(NH_3)_5SO_4]Br$.

Linkage isomerism
- Occurs in the complex compounds which contain ambidentate ligand. *e.g.*, $[Co(NH_3)_5NO_2]Cl_2$ or $[Co(NH_3)_5ONO]Cl_2$

Coordination (position) isomerism
- Exhibited by polynuclear complexes by interchanging the position of ligands. *e.g.*,



Hydrate or solvate isomerism
- Isomerism arises when different number of water molecules are present inside and outside the coordination sphere, *e.g.*, $CrCl_3 \cdot 6H_2O$ exists in three isomeric forms.
$[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]H_2O.Cl_2$, $[Cr(H_2O)_4Cl_2]Cl.2H_2O$

Polymerisation isomerism
- Isomerism arises in the compounds which have same stoichiometric composition but different molecular composition.
$[Pt(NH_3)_2Cl_2]$ and $[Pt(NH_3)_4]$ $[PtCl_4]$

Stereoisomerism

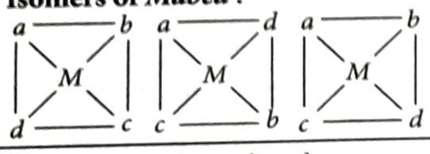
Geometrical

Tetrahedral Complex
Geometrical isomerism is not possible

Square planar complex

Structure	No. of isomers
$Mabcd$	3
$Mabc_2$	2 (*cis-trans*)
Ma_2b_2	2 (*cis-trans*)
$M(ab)_2$	2 (*cis-trans*)

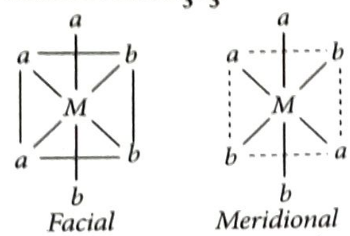
Isomers of $Mabcd$:



Octahedral complex

Ma_2b_4	2 (*cis-trans*)
$M(aa)_2b_2$	2 (*cis-trans*)
$M(aa)_2bc$	2 (*cis-trans*)
Ma_3b_3	2 (*fac/mer*)

Isomers of Ma_3b_3:



Facial or '*fac*'   Meridional or '*mer*'

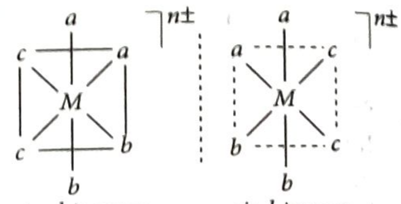
Optical

Tetrahedral complexes : Optical isomerism is possible but no isomer has been isolated.

Square planar complexes : Optical isomerism is not possible.

Octahedral complexes :
Octahedral complexes like $Ma_2b_2c_2$, $Mabcdef$, $[M(AA)_3]^{n\pm}$, $[M(AA)_2a_2]^{n\pm}$ $[M(AA)_2ab]$and $[M(AB)_3]$ show optical isomerism.

Isomers of $[Ma_2b_2c_2]^{n\pm}$:



cis-d-isomer   *cis-l*-isomer

*AA and AB are bidentate ligands.

Bonding in Coordination Compounds

- For explaining the nature of bonding and different properties of coordination compounds such as colour, geometry and magnetic properties, some theories has been developed.

Valence Bond Theory (VBT)

- The central atom uses its number of empty s-, p- and d-atomic orbitals which is equal to its coordination number.
- These empty orbitals hybridise together to form hybrid orbitals.
- The non-bonding electrons of the metal occupy the inner orbitals.
- The d-orbitals participating in the process of hybridization in octahedral complexes may either be $(n-1)d^2sp^3$, inner or low spin complexes or nsp^3d^2 outer or high spin complexes.

Coordination number	Type of hybridization	Geometry	Examples
2	sp	Linear	$[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$
3	sp^2	Trigonal planar	$[HgI_3]^-$
4	sp^3	Tetrahedral	$[Ni(CO)_4]$, $[NiX_4]^{2-}$, $[ZnCl_4]^{2-}$, $[CuX_4]^{2-}$ (where $X = Cl^-, Br^-, I^-$)
	dsp^2	Square planar	$[Ni(CN)_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$ $[Ni(NH_3)_4]^{2+}$
5	sp^3d	Trigonal bipyramidal	$[Fe(CO)_5]$, $[SbF_5]^{2-}$
6	d^2sp^3 or sp^3d^2	Octahedral	$[Cr(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{3-}$ $[FeF_6]^{3-}$, $[Fe(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$

Differences between inner orbital and outer orbital complexes :

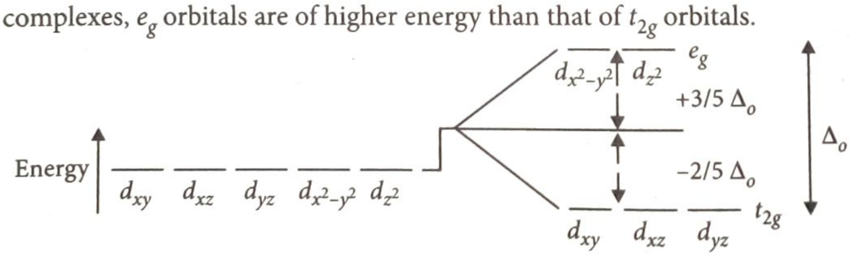
S.N.	Inner orbital octahedral complexes or low spin complexes	Outer orbital octahedral complexes or high spin complexes
1.	The complexes are formed by strong ligands and showing d^2sp^3-hybridisation.	The complexes are formed by weak ligands and showing sp^3d^2-hybridisation.
2.	These complexes generally possess less number of unpaired electrons *i.e.*, they show either low or no magnetic moment.	These complexes generally possess greater number of unpaired electrons *i.e.*, they show high magnetic moment.
3.	These are less reactive *i.e.*, more stable. Substitution reactions are difficult to occur.	These are reactive *i.e.*, less stable. Substitution reactions are easy to occur.

Crystal Field Theory (CFT)

- According to crystal field theory, the bonding in complexes is purely electrostatic.
- The complex is regarded as a combination of a central metal ion surrounded by ligands which act as point charges or point dipoles.
- Interaction between positively charged central metal ion or atom and the negatively charged ligands are of two types.
  - The attractive forces arise due to the positive metal ion and the negatively charged ligands or the negative end of a polar neutral molecules.
  - The repulsive forces arise between the lone pairs on the ligands and electrons in the *d*-orbitals of the metal or atom.
- In a free transition metal or ion, there are five *d*-orbitals which are designated as d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$ and d_{z^2}. The five *d*-orbitals are split into two sets, depending on the nature of their orientation in space. This splitting known as crystal field splitting.
- The splitting is different in different structures with different coordination numbers. The crystal field splitting (Δ_o) depends upon the nature of the ligands. The ligands which cause only a small degree of crystal field splitting are called weak field ligands while those which cause a large degree of splitting are called strong field ligands.

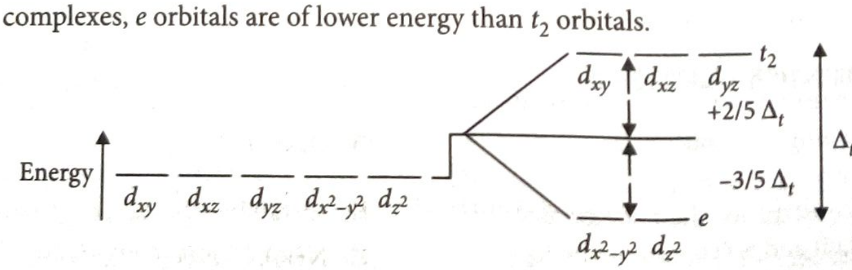
← Strong   Weak →
$CO > CN^- > NO_2^- > en > NH_3 \approx Py > EDTA > H_2O > ox > OH^- > F^- > NO_3^- > Cl^- > SCN^- > Br^- > I^-$
Relative ligand field strengths

- In octahedral complexes, e_g orbitals are of higher energy than that of t_{2g} orbitals.



Splitting of *d*-orbitals in an octahedral complex

- In tetrahedral complexes, *e* orbitals are of lower energy than t_2 orbitals.



Splitting of *d*-orbitals in a tetrahedral complex

Splitting in tetrahedral complexes (Δ_t) is considerably less than in octahedral complexes (Δ_o) *i.e.*, $\Delta_t \approx 4/9\ \Delta_o$

Calculation of CFSE

- In an octahedral complex, each electron occupying t_{2g} orbital results in lowering of energy by $-0.40\ \Delta_o$ (or -4 Dq). Similarly, each electron occupying e_g orbital results in increase of energy by $+0.60\ \Delta_o$ (or $+6$ Dq).
  Thus, CFSE = $(-0.4x + 0.6y)\ \Delta_o$
  where, x = number of electrons occupying t_{2g} orbitals and y = number of electrons occupying e_g orbitals.
  Negative value of CFSE indicates net lowering in energy, *i.e.*, gain in stability.

Calculation of CFSE Values for d^1 to d^{10} Configurations

Metal ion configuration	Low spin state (strong field ligand)	CFSE (Δ_o/Dq)	High spin state (weak field ligand)	CFSE (Δ_o/Dq)
d^1	$t_{2g}^1\ e_g^0$	$-0.4 \times 1 = -0.4\ \Delta_o$ or -4 Dq	$t_{2g}^1\ e_g^0$	$-0.4 \times 1 = -0.4\ \Delta_o$ or -4 Dq
d^2	$t_{2g}^2\ e_g^0$	$-0.4 \times 2 = -0.8\ \Delta_o$ or -8 Dq	$t_{2g}^2\ e_g^0$	$-0.4 \times 2 = -0.8\ \Delta_o$ or -8 Dq
d^3	$t_{2g}^3\ e_g^0$	$-0.4 \times 3 = -1.2\ \Delta_o$ or -12 Dq	$t_{2g}^3\ e_g^0$	$-0.4 \times 3 = -1.2\ \Delta_o$ or -12 Dq
d^4	$t_{2g}^4\ e_g^0$	$-0.4 \times 4 = -1.6\ \Delta_o$ or -16 Dq	$t_{2g}^3\ e_g^1$	$-0.4 \times 3 + 0.6 = -0.6\ \Delta_o$ or -6 Dq
d^5	$t_{2g}^5\ e_g^0$	$-0.4 \times 5 = -2.0\ \Delta_o$ or -20 Dq	$t_{2g}^3\ e_g^2$	$-0.4 \times 3 + 2 \times 0.6 = 0.0\ \Delta_o$ or 0 Dq
d^6	$t_{2g}^6\ e_g^0$	$-0.4 \times 6 = -2.4\ \Delta_o$ or -24 Dq	$t_{2g}^4\ e_g^2$	$-0.4 \times 4 + 2 \times 0.6 = -0.4\ \Delta_o$ or -4 Dq
d^7	$t_{2g}^6\ e_g^1$	$-0.4 \times 6 + 0.6 = -1.8\ \Delta_o$ or -18 Dq	$t_{2g}^5\ e_g^2$	$-0.4 \times 5 + 2 \times 0.6 = -0.8\ \Delta_o$ or -8 Dq
d^8	$t_{2g}^6\ e_g^2$	$-0.4 \times 6 + 2 \times 0.6 = -1.2\ \Delta_o$ or -12 Dq	$t_{2g}^6\ e_g^2$	$-0.4 \times 6 + 2 \times 0.6 = -1.2\ \Delta_o$ or -12 Dq
d^9	$t_{2g}^6\ e_g^3$	$-0.4 \times 6 + 3 \times 0.6 = -0.6\ \Delta_o$ or -6 Dq	$t_{2g}^6\ e_g^3$	$-0.4 \times 6 + 3 \times 0.6 = -0.6\ \Delta_o$ or -6 Dq
d^{10}	$t_{2g}^6\ e_g^4$	$-0.4 \times 6 + 4 \times 0.6 = 0.0\ \Delta_o$ or 0 Dq	$t_{2g}^6\ e_g^4$	$-0.4 \times 6 + 4 \times 0.6 = 0.0\ \Delta_o$ or 0 Dq

Similarly, for tetrahedral complex CFSE = $(-0.6\,x + 0.4\,y)\ \Delta_t$

- The actual configuration adopted by the complex is decided by the relative values of Δ_o and P, where P represents the energy required for electron pairing in a single orbital.
- If Δ_o is less than $P(\Delta_o < P)$, we have weak field, the fourth electron will enter one of the e_g orbitals giving the configuration, $t_{2g}^3\, e_g^1$. It will be high spin complex.
- If Δ_o is more than $P(\Delta_o > P)$, we have strong field and the pairing will occur in the t_{2g} orbitals with e_g orbitals remaining unoccupied giving the configuration, t_{2g}^4. It will be low spin complex.

Stability of Coordination Compounds

- Consider the following reaction
  $M + 4L \rightleftharpoons ML_4$ ...(i)
  The equilibrium constant for the reaction is called the stability constant and is represented by β_4.

$$\beta_4 = \frac{[ML_4]}{[M][L]^4}$$

Larger the stability constant, higher is the proportion of ML_4 that exists in solution.

$$M + L \rightleftharpoons ML\ ; \qquad K_1 = \frac{[ML]}{[M][L]}$$

$$ML + L \rightleftharpoons ML_2\ ; \qquad K_2 = \frac{[ML_2]}{[ML][L]}$$

$$ML_2 + L \rightleftharpoons ML_3\ ; \qquad K_3 = \frac{[ML_3]}{[ML_2][L]}$$

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K_1, K_2 etc. referred to as stepwise stability constants.
Overall stability constant, $\beta_4 = K_1 \times K_2 \times K_3 \times K_4$,

or, $$\beta_4 = \frac{[ML_4]}{[M][L]^4}$$

The instability constant or the dissociation constant of coordination compounds is defined as the reciprocal of the formation constant (stability constant).

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d^{10}	$t_{2g}^6\ e_g^4$	$-0.4 \times 6 + 4 \times 0.6 = 0.0\ \Delta_o$ or 0 Dq	$t_{2g}^6\ e_g^4$	$-0.4 \times 6 + 4 \times 0.6 = 0.0\ \Delta_o$ or 0 Dq

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Organometallic Compounds

Organometallic compounds :
Compounds in which metal is directly attached to carbon, are called organometallic compounds.

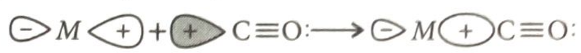
Sigma bonded compounds
Metal carbon bond is sigma bond. *e.g.*, $R-Mg-X$, R_2Zn, $(CH_3)_4Sn$, $(C_2H_5)_4Pb$ etc.

π-bonded compounds
Metal and ligands form a bond that involve π-electrons of ligands. *e.g.*, ferrocene, zeise's salt, etc.

σ and π bonded compounds
These compound possess both σ- and π- bonding between M and ligands. *e.g.*, $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$ etc.

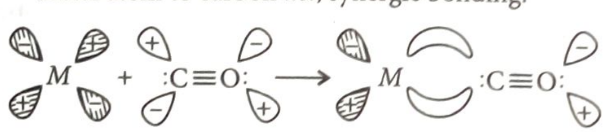
Bonding of Metal Carbonyls

- In a metal carbonyl, the metal-carbon bond possesses both the σ- and π-character. A σ-bond between metal and carbon atoms is formed when a vacant hybrid orbital of the metal atom overlaps with an orbital on C atom of carbon monoxide containing a lone pair of electrons.



Vacant orbital on metal — Lone pair — σ-overlap $M \leftarrow C$ bond

Formation of π-bond is caused when a filled orbital of the metal atom overlaps with a vacant antibonding π^* orbital of C atom of carbon monoxide. This overlap is also called back donation of electrons by metal atom to carbon *i.e.*, synergic bonding.



Filled metal *d*-orbital — Empty π^*2p orbital of CO — $M \rightarrow C$ bond π-overlap

The π-overlap is perpendicular to the nodal plane of σ-bond.

Importance of Coordination Compounds

- In both qualitative and quantitative methods of analysis.
- In metallurgical operations.
- In photography.
- **In electroplating** : Metal complexes release metal slowly and thus give a uniform coating *i.e.*, electroplating of the metal on the desired object.
- **In biological processes :** Coordination compounds are essential in storage and transport of oxygen as electron transfer agents, acts as catalysts and are used in photosynthesis.
- **In medicinal field :** The complex of Ca with EDTA is used for treatment of lead poisoning. *Cis*-platin is used as an antitumor agent.

INFO SHOTS

Some Recent Developments in Coordination Chemistry

Catalysts of the type $(R_3Q)_2MX_2$ (R is an alkyl, aryl, or phenoxy group ; Q is P, As, or Sb ; M is Ni, Pd, or Pt, X is a halogen or halogenoid are recently developed. In the presence of such a substance, polyunsaturated compounds, especially esters of long chain fatty acids are hydrogenated until one double bond remains. The hydrogenation is preceded by *cis-trans* rearrangement of the double bond and migration of the double bonds along the carbon chain ocours for a conjugated system. Another research project has shown that certain bacteria can utilize the nitrogen from *d*-$[Co(en)_3]Cl_3$ but that *l*-$[Co(en)_3]Cl_3$ inhibits their growth.

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Unit 4 — *d*- and *f*-Block Elements | Coordination Compounds

d- AND *f*-BLOCK ELEMENTS

- The *d*-block of the periodic table contains the elements of the group-3 to 12 in which the *d*-orbitals are progressively filled in each of the four long periods.
- In *f*-block, 4*f*- and 5*f*-orbitals are progressively filled. These elements are formal members of group-3 but they have taken out to form a separate *f*-block of the periodic table.

Chemistry of *d*-Block Elements

Elements which have incompletely filled *d*-subshell in their ground state or in any one of their oxidation states, are called *d*-block elements. All the *d*-block elements except Zn, Cd and Hg, are transition elements. These elements have completely filled *d*-subshell in their ions, that is why they are not considered as transition elements.

Electronic Configuration

General configuration : $(n-1)d^{1-10}\,ns^{0-2}$

Here, $(n-1)$ stands for inner shell and n for outermost shell or *s*-orbital.

As half-filled (d^5) and fully filled (d^{10}) configurations are more stable. So, Cr and Cu show exceptional electronic configuration in 3*d*-series.

First Transition Series	Second Transition Series	Third Transition Series	Fourth Transition Series
Sc (21) $\Rightarrow$ [Ar]$3d^1 4s^2$	Y(39) $\Rightarrow$ [Kr] $4d^1 5s^2$	La(57) $\Rightarrow$ [Xe] $4f^0\,5d^1 6s^2$	Ac(89) $\Rightarrow$ [Rn]$5f^0\,6d^1 7s^2$
Ti (22) $\Rightarrow$ [Ar]$3d^2 4s^2$	Zr(40) $\Rightarrow$ [Kr] $4d^2 5s^2$	Hf(72) $\Rightarrow$ [Xe]$4f^{14} 5d^2 6s^2$	Rf(104) $\Rightarrow$ [Rn] $5f^{14}\,6d^2 7s^2$
V(23) $\Rightarrow$ [Ar]$3d^3 4s^2$	Nb(41) $\Rightarrow$ [Kr]$4d^4 5s^1$	Ta(73) $\Rightarrow$ [Xe]$4f^{14} 5d^3 6s^2$	Db(105) $\Rightarrow$ [Rn] $5f^{14}\,6d^3 7s^2$
Cr(24) $\Rightarrow$ [Ar]$3d^5 4s^1$	Mo(42) $\Rightarrow$ [Kr]$4d^5 5s^1$	W (74) $\Rightarrow$ [Xe] $4f^{14} 5d^4 6s^2$	Sg(106) $\Rightarrow$ [Rn]$5f^{14}\,6d^4 7s^1$
Mn(25) $\Rightarrow$ [Ar]$3d^5 4s^2$	Tc(43) $\Rightarrow$ [Kr]$4d^5 5s^2$	Re(75) $\Rightarrow$ [Xe]$4f^{14} 5d^5 6s^2$	Bh(107) $\Rightarrow$ [Rn]$5f^{14}\,6d^5 7s^2$
Fe(26) $\Rightarrow$ [Ar]$3d^6 4s^2$	Ru(44) $\Rightarrow$ [Kr]$4d^7 5s^1$	Os(76) $\Rightarrow$ [Xe] $4f^{14} 5d^6 6s^2$	Hs(108) $\Rightarrow$ [Rn] $5f^{14}\,6d^6 7s^2$
Co(27) $\Rightarrow$ [Ar]$3d^7 4s^2$	Rh(45) $\Rightarrow$ [Kr]$4d^8 5s^1$	Ir(77) $\Rightarrow$ [Xe] $4f^{14} 5d^7 6s^2$	Mt(109) $\Rightarrow$ [Rn] $5f^{14}\,6d^7 7s^2$
Ni(28) $\Rightarrow$ [Ar]$3d^8 4s^2$	Pd(46) $\Rightarrow$ [Kr]$4d^{10} 5s^0$	Pt(78) $\Rightarrow$ [Xe] $4f^{14}\,5d^9 6s^1$	Ds(110) $\Rightarrow$ [Rn]$5f^{14} 6d^9 7s^1$
Cu(29) $\Rightarrow$ [Ar]$3d^{10} 4s^1$	Ag(47) $\Rightarrow$ [Kr]$4d^{10}\,5s^1$	Au(79) $\Rightarrow$ [Xe] $4f^{14}\,5d^{10} 6s^1$	Rg(111) $\Rightarrow$ [Rn]$5f^{14} 6d^{10} 7s^1$
Zn(30) $\Rightarrow$ [Ar]$3d^{10} 4s^2$	Cd(48) $\Rightarrow$ [Kr]$4d^{10} 5s^2$	Hg(80) $\Rightarrow$ [Xe] $4f^{14} 5d^{10} 6s^2$	Cn(112) $\Rightarrow$ [Rn]$5f^{14} 6d^{10} 7s^2$

General Properties of *d*-Block Elements

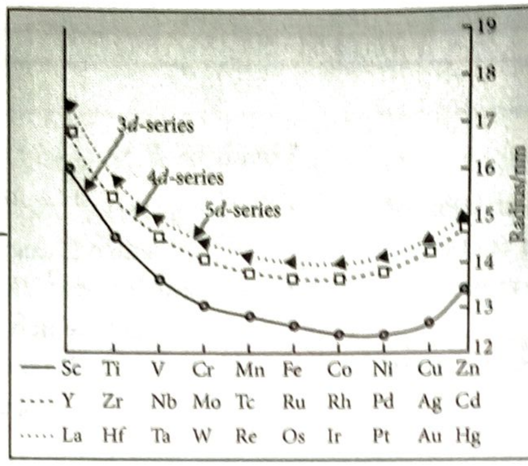
Metallic Character

Due to presence of strong metallic bonds, the transition metals are hard, possess high densities and high enthalpies of atomisation. Scandium has least density whereas Iridium has the highest density among the transition metals.

Atomic and Ionic Sizes

Trends in atomic radii of transition elements

The atomic radii first decreases, at the middle becomes almost constant and then increases towards the end of the period.
In first transition series, atomic radii decrease from Sc to Cr, remain almost constant till Cu and then increase.



The elements of second and third transition series belonging to a particular group have almost equal atomic radii. This is due to the intervention of the 4*f*-orbitals which must be filled before the 5*d* series of elements begins. The filling of 4*f*-orbitals before 5*d*-orbitals results in a regular decrease in atomic radii known as **lanthanoid contraction**.

Ionisation Enthalpy

- The ionisation enthalpy of *d*-block elements are higher than those of *s*-block elements and are lower than those of *p*-block elements.
- In a particular transition series, ionisation enthalpy increases gradually but quite slowly among *d*-block elements.
- Extra stability of half filled and fully filled orbital give rise to high ionisation enthalpy.

Oxidation state

- Variable oxidation states arise due to participation of $(n - 1)d$ and *ns*-electrons.
- The element which shows the greatest number of oxidation state occur in or near the middle of the series, *e.g.*, Mn
- In + 2 and +3 oxidation states, the bonds formed are mostly ionic.
- In a group of *d*-block elements, the higher oxidation states are more stable for heavier elements.
- Low oxidation states such as +1, 0 or negative are also possible.

Sc	$+\underline{3}$
Ti	(+ 2), + 3, $+\underline{4}$
V	+ 2, + 3, + 4, $+\underline{5}$
Cr	(+1), + 2, + 3, (+ 4), (+ 5), $+\underline{6}$
Mn	$+\underline{2}$, + 3, + 4, (+ 5), + 6, + 7
Fe	+ 2, $+\underline{3}$, (+ 4), (+ 5), (+ 6)
Co	$+\underline{2}$, + 3, (+4)
Ni	$+\underline{2}$, + 3, + 4
Cu	+ 1, $+\underline{2}$
Zn	$+\underline{2}$

Y	$+\underline{3}$
Zr	(+ 3), $+\underline{4}$
Nb	(+ 2), $+\underline{3}$, (+ 4), + 5
Mo	+ 2, + 3, + 4, + 5, $+\underline{6}$
Tc	+ 2, $+\underline{4}$, (+ 5), $+\underline{7}$
Ru	+2, + 3, $+\underline{4}$, (+ 5), (+ 6), (+ 7), (+ 8), 0, –2
Rh	+ 2, $+\underline{3}$, $+\underline{4}$, (+ 6)
Pd	$+\underline{2}$, (+ 3), +4
Ag	$+\underline{1}$, (+ 2), (+ 3)
Cd	$+\underline{2}$

La	$+\underline{3}$
Hf	(+ 3), $+\underline{4}$
Ta	(+ 2), (+ 3), (+ 4), $+\underline{5}$
W	+ 2, (+ 3), + 4, + 5, $+\underline{6}$
Re	(– 1), (+ 1), (+ 2), $(+\underline{3})$, + 4, + 5, (+ 6), $+\underline{7}$
Os	+ 2, + 3, $+\underline{4}$, + 6, $+\underline{8}$
Ir	+ 2, + 3, $+\underline{4}$, (+ 6)
Pt	+ 2, (+ 3), $+\underline{4}$, (+ 5), (+ 6)
Au	+ 1, $+\underline{3}$
Hg	+1, $+\underline{2}$

*Oxidation states, which are in brackets, are unstable while underlined oxidation states are stable.

Standard Reduction Potential

- Lower the electrode potential *i.e.*, more negative the standard reduction potential of the electrode, more stable is the oxidation state of the transition metal in the aqueous medium.

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$E^\circ_{(M^{2+}/M)}$ in volts (V)	—	–1.63	–1.18	–0.91	–1.18	–0.44	–0.28	–0.25	+0.34	–0.76
$E^\circ_{(M^{3+}/M^{2+})}$ in volts (V)	–2.08	–0.37	–0.26	–0.41	+1.57	+0.77	+1.97	—	—	—

Trends in $E^\circ_{M^{2+}/M}$:
- No regular trend due to irregular variation of ionisation energies and sublimation energies.
- Except copper, all other elements have negative reduction potential values.
- The values of E° for Mn, Zn and Ni are more negative than expected from general trend.

Trends in $E^\circ_{M^{3+}/M^{2+}}$:
- E° value for Sc^{3+}/Sc^{2+} is very low reflect the stability of Sc^{3+} which is due to noble gas configuration.
- E° value for Mn^{3+}/Mn^{2+} is high shows that Mn^{2+} is very stable which is due to d^5 configuration.
- E° values for the redox couple M^{3+}/M^{2+} indicate Mn^{3+} and Co^{3+} are strongest oxidising agents.

SOME MORE PROPERTIES

Formation of Interstitial Compounds
- Small non-metallic atoms such as, H, B, C, N etc. are able to occupy interstitial spaces of the lattices of the *d*-block elements to form interstitial compounds.

Colour
- Most of the compounds of transition metals are coloured in the solid as well as in aqueous solution.
- Colour arises due to *d-d* transition.
- Transition elements with completely filled or completely empty *d*-orbitals are colourless, *e.g.*, Cu^+, Ag^+, Au^+, Zn^{2+}, Cd^{2+}, etc.

Catalytic properties
- Catalytic properties are due to unpaired electrons in their *d*-orbitals, *e.g.*, V_2O_5, cobalt, Ni, etc.

Tendency to form complexes
Due to small size, high nuclear charge and vacant *d*-orbitals they can accept lone pairs of electrons donated by the ligands, *e.g.*, $[Fe(CN)_6]^{3-}$, etc.

Magnetic properties
- Most of the compounds are paramagnetic due to presence of unpaired electrons.
- $\mu_{eff} = \sqrt{n(n+2)}$ B.M. where, n = number of unpaired electrons.
- Magnetic moment first increases from d^1 to d^5 and then decreases.

Alloy formation
Due to similar atomic radii and other characteristics, they form alloy very readily.

Some Important Compounds of *d*-Block Elements

Potassium Dichromate ($K_2Cr_2O_7$)	Potassium Permanganate ($KMnO_4$)
Preparation : $Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$	**Preparation :** $2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$ $3K_2MnO_4 + 4HCl \longrightarrow 2KMnO_4 + MnO_2 + 2H_2O + 4KCl$
Properties : • Orange coloured crystalline compound which is soluble in water. • On strong heating, it decomposes with the evolution of oxygen. $4K_2Cr_2O_7 \longrightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$ • On heating with alkalies, a yellow solution results due to formation of chromate. $\underset{\text{(Orange)}}{K_2Cr_2O_7} + 2KOH \longrightarrow \underset{\text{(Yellow)}}{2K_2CrO_4} + H_2O$ • In the solution, dichromate ions exist in equilibrium with chromate ions. $\underset{\text{(Orange)}}{Cr_2O_7^{2-}} + H_2O \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} \underset{\text{(Yellow)}}{2CrO_4^{2-}} + 2H^+$; pH = 4 • In acidic medium, it acts as a strong oxidising agent. $\overset{(+6)}{Cr_2O_7^{2-}} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ • **Chromyl chloride test :** Test for chloride ion. When a mixture of a metal chloride and potassium dichromate is heated with conc. H_2SO_4, orange-red vapours of chromyl chloride are evolved. $K_2Cr_2O_7 + 6H_2SO_4 + 4NaCl \longrightarrow 2KHSO_4 + 4NaHSO_4 + \underset{\text{chromyl chloride}}{2CrO_2Cl_2} + 3H_2O$ $CrO_2Cl_2 + 4NaOH \longrightarrow \underset{\text{Yellow soln.}}{Na_2CrO_4} + 2NaCl + 2H_2O$ $Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow 2CH_3COONa + \underset{\text{Yellow ppt.}}{PbCrO_4}$	**Properties :** • Deep purple coloured crystalline solid, moderately soluble in water. • On heating, it decomposes to give O_2. $2KMnO_4 \xrightarrow[513\ K]{\Delta} K_2MnO_4 + MnO_2 + O_2$ • With conc. H_2SO_4, it gives Mn_2O_7 which on heating decomposes to MnO_2. $2KMnO_4 + 2H_2SO_4 \longrightarrow 2KHSO_4 + Mn_2O_7 + H_2O$ $2Mn_2O_7 \xrightarrow{\Delta} 4MnO_2 + 3O_2$ • In alkaline solution, it acts as an oxidising agent. $2KMnO_4 + H_2O \xrightarrow{\text{Weakly alkaline}} 2MnO_2 + 2KOH + 3[O]$ • In neutral solution, it acts as a moderate oxidising agent. $2KMnO_4 + H_2O \longrightarrow 2MnO_2 + 2KOH + 3[O]$ • In acidic solution, it acts as a strong oxidising agent. $2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$
Uses : • As a volumetric reagent. • Preparation of several chromium compounds. • In dyeing, chrome tanning, photography, etc.	**Uses :** • As a strong oxidising agent in laboratory. • Alkaline potassium permanganate is known as Baeyer's reagent used for the testing unsaturation. • As a disinfectant and germicide.